

PBDEs and HBCD in Marine Sediments from the North Sea, Germany

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Introduction

The OSPAR-Commission, who is implementing the Convention on the Protection of the Marine Environment of the North-Atlantic Ocean, has developed a Hazardous Substances Strategy (www.ospar.org) with the objective of preventing pollution of the maritime area by continuously reducing discharges, emissions and losses of hazardous substances. The ultimate aim is to achieve pollution levels in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances by the year 2020. OSPAR has identified 48 chemicals for priority action and has listed 325 further substances of possible concern. For most of these substances it is not known whether they reach the marine environment and in which concentrations they might occur in water, sediment and biota. Therefore, some of these chemicals including short- and medium-chain chlorinated paraffins, chlordanes, endosulfanes, chlorpyrifos, trifluralin, polybrominated diphenyl ethers (PBDE), and hexabromocyclododecane (HBCD) were monitored in marine samples from the North Sea to assess the relevance of these substances to the marine environment (e.g. Lepom et al. 2006). A few studies on DecaBDE concentrations in the aquatic environment identified this fully brominated BDE congener in high concentrations in sediment samples from diverse locations (Law et al. 2006). Moreover, there are a few recent reports on the occurrence of HBCD, another high-production volume brominated flame retardant, in the marine environment (Covaci et al. 2006). Here we report the results of a four year study of a total of 14 BDE congeners and HBCD determined in marine sediments collected at 13 locations in the German North Sea using a fully optimised and validated GC-ECNI-MS method.

Materials and Methods

Sampling was performed following the JAMP Guidelines for Monitoring Contaminants in Sediments (OSPAR, 1997). The sampling stations were selected for a most comprehensive and representative coverage of the sea areas under investigation (Figure 1). Oceanographic parameters (sea currents), inflow from big rivers as well as sediment characteristics were taken into account. In addition, two locations (S01, S02) represent former sewage sludge dumping sites while another one (S04) was a titanium dioxide dumping site. Sediment samples were taken in 2002 to 2005 using a box corer capable of sampling surface sediments without disturbing their structure. The upper layers of the sediments ranging from 0 to 2 cm were transferred with a metal spatula into aluminium boxes and immediately frozen at -20°C. Until analysis samples were kept at that temperature. All samples were air-dried in a clean-bench, then grinded in a ball mill and homogenised.

A modified analytical procedure described previously was employed (Sawal et al. 2005). In brief, 10 to 20 g of air-dried sediments were extracted with toluene in the presence of copper four times using a ASE-system (Dionex Corporation, Sunnyvale, CA, U.S.A.) operated at 125°C and 14 MPa. In some cases extracts required an additional treatment with activated copper granules to remove residual sulphur. The obtained extract was cleaned-up by gel permeation chromatography followed by multi-layer column chromatography (silica gel/acid-impregnated silica gel). Quantification of BDEs 28, 47, 66, 71, 75, 85, 99,

100, 138, 153, 154, 183, 190, 209 and HBCD was performed by capillary gas chromatography-electron capture negative ionisation mass spectrometry (GC-ECNI-MS) in the selected ion monitoring mode under the following conditions: GC 6890+ / MSD 5973 (Agilent, Palo Alto, CA, U.S.A.) equipped with autosampler MPS2 (CTC Analytics AG, Switzerland) and PTV injector KAS 4 plus (Gerstel, Mülheim/Ruhr, Germany); capillary column: Rtx-CLPesticides (Restek, Bellefonte, PA, U.S.A.), 30 m x 0.25 mm, film thickness: 0.25 µm; pressure-pulse injection, injection volume: 2 µl; carrier gas: helium; CI ion source, reagent gas: methane; ion source temperature: 210°C. BDEs elute from the column under these conditions between 11 and 35 minutes. For congeners with three to seven bromine atoms the most prominent ions due to bromine at $m/z = 79$ and $m/z = 81$ were recorded, while for the decabromodiphenyl ether (BDE209) the highly specific ions at $m/z = 484.7$ and $m/z = 486.7$ were monitored. The monofluorinated BDEs FBDE28, FBDE100, and FBDE160 as well as BDE181 and ^{13}C -labelled BDE209 were used as internal standards. Fluorinated BDEs were purchased from Chiron AS, Trondheim, Norway, all other standards were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada.). QA/QC included replicate sample analyses, regular analyses of procedural blanks, analysis of reference materials (QUASIMEME QBC003MS) and participation in international interlaboratory studies on the determination of PBDEs in sediments (QUASIMEME and NIST). Average procedural blank values were considered in the quantification of BDE47 and BDE209.

The total organic carbon content (TOC) of the sediments was determined in suspension using a Shimadzu TOC-V_{CPN}-System. It was assumed that the non-purgeable organic carbon detected with this method represents the TOC of the sediments. The certified reference material NIST 1941b, Organics in Marine Sediments, was used as quality control sample.

Results and Discussion

BDE patterns in all marine sediment samples were dominated by decabromodiphenyl ether (DecaBDE, BDE209), which was found in all samples from the North Sea, followed by BDE99 and BDE47. However, concentrations of summed tri- to hexabrominated congeners representative for the technical penta-formulation were fairly low, often only BDE47 and BDE99 were detected. BDE 209 contributed on the average $89 \pm 6\%$ to the total amount of BDEs in the sediment samples, which is in line with previously reported BDE congener patterns for marine and estuarine sediments from Western Europe (Christensen & Platz 2001; Zegers et al. 2003, Voorspels et al. 2004). There was a large variation in the BDE 209 concentrations of the sediment samples from different locations while no statistically significant trends were seen in BDE209 levels of samples taken at the same location in the period 2002 to 2005. Hence, median concentrations of BDE209 for all locations were presented both in ng/g dry weight (Figure 1A) and in ng/g organic carbon (Figure 1B).

BDE209 concentrations in sediments from the North Sea ranged from 0.03 to 6.5 ng/g dry weight. Highest levels were seen in the German Bight at former sewage sludge dumping sites (S01, S02) and in muddy sediments taken off the coast of the Island of Sylt (S05). Sandy sediments (TOC < 0.2%) from the Wadden Sea and the central North Sea (S04, S06, S07, S08, S12, S13) showed the lowest BDE209 concentrations. The DecaBDE levels found in this study correspond to DecaBDE concentrations reported previously for marine sediments from Denmark and the Southern North Sea (n.d. to 3.9 ng/g dw), respectively (Christensen & Platz 2001, Voorspels et al. 2004 and Klamer et al. 2005). Higher levels, 22 to 32 ng/g d.w., were only found in sediments impacted by industrial activity such as those from Copenhagen harbour and Western Scheldt. BDE209 concentrations seen in sediments from various locations in the German North Sea were levelled off by normalising concentrations to the total organic

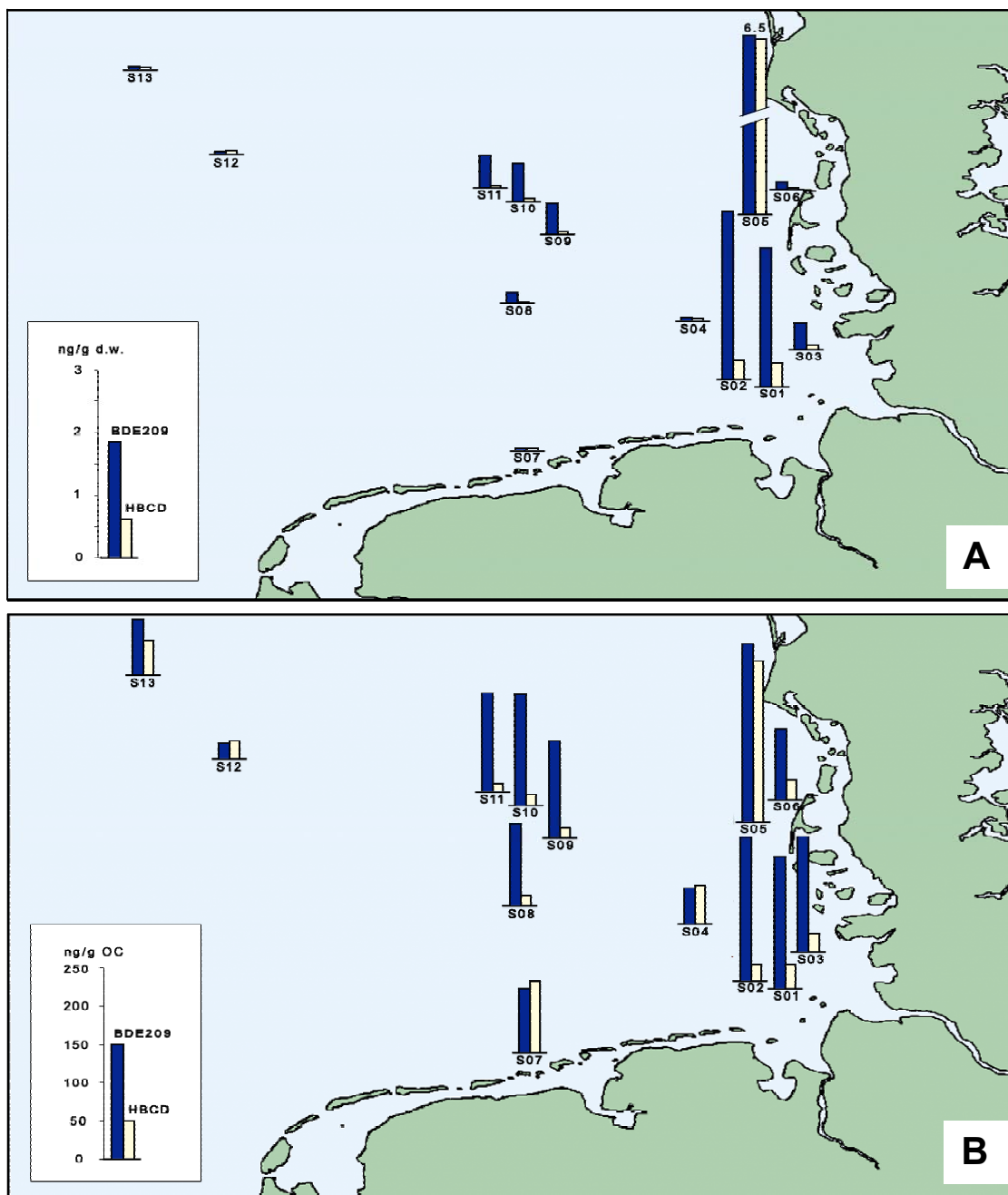


Figure 1. Median concentrations of BDE209 and HBCD in sediment samples taken in the German North Sea expressed in ng/g dry weight (A) and ng/g organic carbon (B). Samples were collected in three or four consecutive years in the period 2002 to 2005 except at stations S05 and S13 where samples were taken only in 2003. Dark and light bars represent BDE209 and HBCD, respectively.

carbon content of the sediments. This indicates that differences seen in dry weight concentrations of BDE209 were partly due to differences in organic carbon content of the sediments and do not solely reflect differences in the contamination level. Most samples showed median DecaBDE levels between 100 and 200 ng/g OC (Figure 1B). These findings are in good agreement with results of sediment core analysis from Western Wadden Sea, which indicated a BDE209 concentration of 250 ng/g OC in the uppermost layer dated to 1995 (Zegers et al 2003). The PBDEs detected in sediment samples can have been transported either via the atmosphere or via water currents and suspended particles. As some stations in the German Bight and in the Wadden Sea are located close to the coast they might be impacted by industrial areas. Thus, PBDE input from local sources via the dissolved phase or suspended particles cannot be excluded, even though BDE levels in sediments from the estuary of River Elbe, the major river draining into the study area, are among the lowest reported in Western Europe (Sawal et al. 2004). In view of this, diffuse input of DecaBDE appears to be the most important input route.

Median HBCD concentrations in the studied North Sea sediments ranged from 0.03 to 0.37 ng/g d.w. corresponding to 10 to 93 ng/g OC for all except one sample and were normally clearly lower than those of BDE 209. The maximum HBCD concentration of 6.5 ng/g d.w. (240 ng/g OC) was found in the muddy sediment collected at station S05. There is only a few data on the occurrence of HBCD in marine sediments showing fairly low HBCD concentrations. Mean HBCD levels of 3.2 (n = 9, <0.8 to 9.9) and 3.4 (n=10; <0.2 to 6.9) ng/g d.w. were reported for coastal sediments from the Western Scheldt and the Southern North Sea with highest concentrations at the river mouth (Zegers et al. 2004, Klamer et al 2005). HBCD concentrations in sediments (fraction < 0.63 µm) from the open Sea were <0.2 to 1.0 ng/g d.w. (Klamer et al. 2005).

Acknowledgements

We gratefully acknowledge Margot Muntermann, Federal Environment Agency, for her valuable technical assistance with sample analysis and TOC determination.

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